Stereochemical Kinetics of Polymerization of Methyl Methacrylate under Group-Transfer Polymerization Conditions. ^{13}C NMR Analysis of Poly(methyl methacrylate) Terminated with Labeled End Groups

Krishna G. Banerjee and Thieo E. Hogen-Esch*

Department of Chemistry and Macromolecular Science, University of Florida, Gainesville, Florida 32611

Received March 8, 1993; Revised Manuscript Received January 14, 1994•

ABSTRACT: The stereochemistry of the chain end of poly(methyl methacrylate) prepared under group-transfer polymerization conditions and terminated with $^{13}CH_3I$ in the presence of tris(dimethylamino)-sulfonium difluorotrimethylsiliconate ($TASSiMe_3F_2$) is determined by ^{13}C NMR and compared with the tacticity of the chain. The propagation statistics reveal consistency with a Bernoullian process for the entire temperature range studied (−96 to +45 °C), confirming previous reports based on main-chain triad tacticity alone. The results suggest that the *E* and *Z* stereoisomers demonstrated for these systems propagate with identical stereochemistry and show that a comparison of the stereochemistry of the end group and the main chain is a valuable method for analyzing the stereochemical statistics of vinyl polymerization.

Introduction

The polymerization of acrylic monomers initiated by the addition of a small amount of a nucleophilic catalyst to a silylketene acetal initiator is referred to as group-transfer polymerization (GTP).[1-6] The polymerization has been shown to have many of the characteristics of "living" polymerizations and allows the synthesis of relatively narrow molecular weight distribution polymers whose number-average molecular weights are controlled by the mole ratio of monomer to initiator. The temperature dependence of the tacticity of poly(methyl methacrylate) (PMMA) prepared by GTP has been reported, and propagation statistics have been shown to be consistent with Bernoullian statistics.[3,5]

E and *Z* geometric isomers have been shown to participate as intermediates in the anionic polymerization of MMA,[7] 2-vinylpyridines,[8,9] and related monomers, and (*E*)- and (*Z*)-silylketene acetals have also been demonstrated as intermediates in the GTP of MMA.[10]

Since (*E*)- and (*Z*)-silylketene acetals are geometric isomers, it may be expected that they show a different stereochemistry of monomer addition. A model based on the simultaneous participation of *E* and *Z* isomers in polymerization has been shown to generally lead to non-Bernoullian statistics although this model reduces to Bernoullian statistics under certain limiting conditions.[11] Hence, the reports[3,5] that the statistics of GTP of MMA are consistent with a Bernoullian process were surprising to us. We therefore decided to verify the above reports by our independent and sensitive method involving the comparison of main-chain and chain-end stereochemistry, which has been previously developed in our laboratory.[12-14] In this paper, we report on the temperature dependence of the tacticity of both the main chain and the chain end as determined by ^{13}C NMR of a labeled end group, confirming the occurrence of Bernoullian statistics.

* To whom correspondence should be addressed at the Department of Chemistry, University of Southern California, University Park, Los Angeles, CA 90089-1661.

• Abstract published in *Advance ACS Abstracts*, March 1, 1994.

Experimental Section

Monomers and Catalysts. Methyl methacrylate (MMA; Aldrich) was purified by distilling twice from calcium hydride and once from triethylaluminum under vacuum. It was stored in ampules equipped with breakseals in a freezer (−20 °C). The initiator, ((1-methoxy-2-methyl-1-propenyl)oxy)trimethylsilane (Aldrich), was distilled from calcium hydride under high vacuum and stored as a THF solution in ampules equipped with breakseals at room temperature. Tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) was prepared according to the literature procedure[1-3] and stored as an acetonitrile solution under argon. Tetrahydrofuran (THF) was refluxed over sodium and potassium metal, distilled onto fresh alloy, degassed, and stored under high vacuum with benzophenone. It was distilled in the reaction flask prior to use. ^{13}C-labeled methyl iodide (Aldrich; 99 atom % ^{13}C) was distilled from calcium hydride into the reaction flask. Tris-(dimethylamino)sulfonium difluorotrimethylsiliconate ($TASSiMe_3F_2$; Aldrich, technical grade containing 10% $TASHF_2$) was used without further purification. It was stored dry under argon and added as an acetonitrile solution prior to use. Tris-(diethylamino)sulfonium difluorotrimethylsiliconate ($EtTASiMe_3F_2$) was prepared according to a patent procedure.[15] A dark brown oil was the final product, which even after continuous evacuation at high vacuum (10^{-6} Torr) for more than 24 h did not yield the expected solid. Analysis by ^1H, ^{13}C, and ^{19}F NMR revealed the presence of a mixture of $EtTASiMe_3F_2$ and $EtTASHF_2$ in *ca.* 85:15 ratio in quantitative yield. The NMR characterization yielded the following results (ppm):

NMR (^{13}C, THF-d_8, 50 MHz): 7.3 ($SiCH_3$), 13.2 (NCH_2CH_3 of $((Et_2N)_3SSiMe_3F_2)$, 42.0 (NCH_2 of $(Et_2N)_3SSiMe_3F_2$), 14.7 (NCH_2CH_3 of $(Et_2N)_3SHF_2$), 38.7 (NCH_2 of $(Et_2N)_3SHF_2$).

NMR (^1H, THF-d_8, 200 MHz): 0.0 (s, $SiCH_3$), 1.28 (t, NCH_2CH_3 of HF_2), 1.43 (t, NCH_2CH_3 of $(Et_2N)_3SSiMe_3F_2$), 3.22 (q, NCH_2 of $(Et_2N)_3SHF_2$), 3.54 (q, NCH_2 of $(Et_2N)_3SSiMe_3F_2$).

NMR (^{19}F, THF-d_8, 188 MHz, $CFCl_3$ = 0.00 ppm): −57.00 (s, $(Et_2N)_3SSiMe_3F_2$), −149.8 (d, J_{HF} = 120 Hz, $(Et_2N)_3SHF_2$).

Quantitative determination of the products resulting from the methylation of the initiator was determined using a Hewlett-Packard Model 5880A gas chromatograph equipped with a capillary column and a flame ionization detector.

Group-Transfer Polymerizations. Method A. Polymerization was carried out under high-vacuum conditions. An acetonitrile solution of $TASHF_2$ (0.25–0.5 mol % with respect to the initiator) was first added to the reaction vessel, and the solvent was pumped off. After distillation of THF into the reaction vessel

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and addition of the initiator, MMA was added during vigorous stirring by slow vapor phase distillation into the reaction flask, which was maintained at a constant temperature.

Method B. This procedure is identical to procedure A except that the monomer was added *in vacuo*.

Method C. In this case, a mixture of monomer and initiator was added slowly *in vacuo* to a suspension of the catalyst in THF.

Method D. This procedure was identical to that of method C except that the polymerization was carried out under argon.

Methylation of chain ends was accomplished by addition of $^{13}CH_3I$ (99%) to the polymerization mixture, followed by 1 equiv of $TASSiMe_3F_2$ under argon. The temperature of methylation was −78 or 0 °C. The temperature of methylation was shown to have no effect on chain-end tacticity but had a slight effect on the stereochemistry of methylation.

Isolation of Polymers. The polymers were isolated by first extracting with water/chloroform. The TASI salt was removed in the aqueous layer. The chloroform layer containing the methylated PMMA was dried with anhydrous sodium sulfate and filtered. It was then precipitated with excess (*ca.* 10/1 (v/v)) cyclohexane or hexanes, collected by vacuum filtration, and dried *in vacuo* at 50 °C.

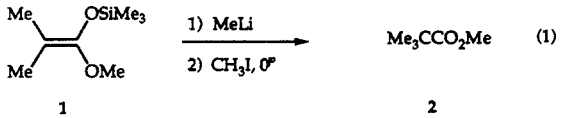
Polymer Characterization. NMR characterization of PMMA stereochemistry was carried out on a Varian 200 XL (200 MHz) spectrometer in either $CDCl_3$ (50 °C) or tetrachloroethane-d_2 at 90 °C at concentrations of ~200 mg/mL of solvent. The triad tacticities of the chain were determined both by integration of the α-methyl protons (0.7–1.3 ppm) and by integration of the α-methyl carbon signals (17–23 ppm). The triad fractions of the chain end were calculated from the upfield and downfield ^{13}C NMR signals at 23–24 and 29–30 ppm,[16,17] respectively, corresponding to the diastereotopic labeled end groups. The relative areas of the peaks were determined by electronic integration and/or by direct determination of the relative peak areas (in the NMR spectrum).

Molecular weights and molecular weight distributions were measured by size exclusion chromatography (SEC) on a Waters Model 6000A liquid chromatograph with THF as eluent. Flow rates were typically 0.7–1.5 mL/min. Both refractive index and UV detectors were used. Phenomenex TSK G3000 (7.8 mm × 30 cm; 10^3 Å) and TSK G5000HXL (10^5 Å) columns in series following TSK guard columns were used. The column set was calibrated with PMMA standards (Polymer Standards Services, Mainz, Germany).

Results and Discussion

Since the chain end of PMMA prepared under GTP conditions is a silylketene acetal, the addition of alkylating agents such as $^{13}CH_3I$ is not expected to result in chain-end methylation. Unlike the polymerization, the methylation is not expected to occur with the addition of a small amount of an appropriate catalyst.[1,2]

Therefore, we carried out some model studies with the silylketene acetal initiator **1**. Addition of 1 equiv of methyllithium to a THF solution of **1** at −78 °C followed by addition of $^{13}CH_3I$ failed to give methylation after 7 h at −78 °C. However, addition of MeLi at 25 °C followed by MeI at 0 or −78 °C gave methyl pivalate (**2**) together with several unidentified products (eq 1). However, this



(1)

1 **2**

method failed to give chain-end methylation for the case of GTP of MMA. Apparently, competing side reactions of MeLi with the ester group(s) of the chain were too rapid in this case. We therefore tried the addition at −78 °C in THF of 1 equiv of $TASSiMe_3F_2$ in the presence of excess $^{13}CH_3I$ following a similar procedure involving the benzylation of PMMA prepared by GPT.[1c] Following Noyori,[18,19] this reaction proceeds through a TAS enolate (Scheme 1).

Scheme 1. Methylation of the PMMA Silylketene Acetal

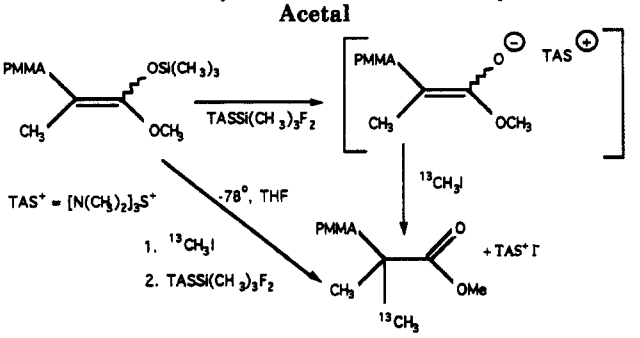


Table 1. Product Distribution Resulting from Reaction of Initiator (1) with $TASSiMe_3F_2$ and $EtTASSiMe_3F_2$

run	mol of 1 (×10)	mol of $TASSiMe_3F_2$ (×10)	mol of $EtTASSiMe_3F_2$ (×10)	mol of 2 (×10)
1	0.60		0.73	0.57
2	0.73		0.37	0.41
3	2.18	1.74		1.23
4	0.60	1.05		0.28

The methylation of the GTP initiator with $TASSiMe_3F_2$ was sometimes not reproducible, presumably as a result of the insolubility of the catalyst in THF (run 4, Table 1). Reversing the order of addition of the reagents (*i.e.*, $TASSiMe_3F_2$ first and then $^{13}CH_3I$) fails to give methylation of the PMMA chain end. Presumably, this is due to rapid competing side reactions of the very reactive TAS enolate species, resulting ultimately in protonation of the active center. Methylation experiments with the GTP initiator using the crude THF-soluble $EtTASSiMe_3F_2$ and methyl iodide with vinyl pivalate as a GC internal standard showed that the yield of the methylated product (**2**) corresponded approximately to the moles of the siliconate (Table 1). Thus when $EtTASSiMe_3F_2$ catalyst was used in slight molar excess compared to the initiator, with an excess of methyl iodide (~2–3 equiv compared to the initiator) the yield of methylated product was essentially quantitative (run 1). When the catalyst was used in amounts of <1 equiv compared to the initiator, the yield of methyl pivalate (**2**) reflected approximately the proportion of the catalyst.

The results are consistent with the view that the alkylation proceeds through a TAS enolate species formed by a 1:1 reaction of the initiator and the polymerization catalyst. In the above methylation experiments, both methyl pivalate and TASI were isolated and characterized, the former by ^1H and ^{13}C NMR and the latter by C,H,N analysis.

Table 2 summarizes the experimental conditions of the polymerization reactions of MMA and the results obtained from SEC analysis. The reasons for employing methods C and D in some of these polymerizations were the frequent low yields due to incomplete monomer conversion obtained at 0 °C and higher temperatures when monomer was slowly added to the initiator and catalyst (method B). This is apparently due to competing side reactions involving both the initiator or chain-end silylketene acetal and catalyst (possibly between an initiator–catalyst complex and initiator or between an initiator–catalyst complex and the catalyst) resulting in the protonation of the initiator or chain end. The rates of side reactions must be lower than the polymerizations rates, however, on account of the excellent yields and good molecular weight control at lower temperatures (runs 1–5, Table 2). In addition, the side

Table 2. Experimental Conditions and SEC Results of PMMA Prepared under GTP Conditions in THF

expt no.	T/°C	M_n[e] (calc)	M_n	M_w	M_w/M_n	yield[f]/%
1[a]	−96	2255	1847	2390	1.29	>98
2[a]	−85	2460	2024	2782	1.37	>98
3[a]	−78	1800	1602	1929	1.20	>98
4[a]	−40	2200	1944	2220	1.14	>98
5[a]	−23	2915	3172	4198	1.32	>98
6[b]	0	2050	1662	1796	1.08	23
7[c]	25	1500	2799	3917	1.40	91
8[d]	45	1200	2520	3324	1.32	70

[a] Monomer distilled into mixture of initiator + catalyst *in vacuo* (method A; see Experimental Section). [b] Monomer poured slowly into initiator + catalyst mixture *in vacuo* (method B). [c] Initiator and monomer mixture added slowly to catalyst *in vacuo* (method C). [d] Initiator + monomer mixture added to catalyst under argon (method D). [e] Number-average molecular weight calculated from mole ratio of monomer to initiator. [f] Based on weight of polymer isolated.

reactions at higher temperatures can be avoided by changing the order of adding the reagents for the polymerization, *i.e.*, by adding the catalyst to a mixture of initiator and monomer (batch polymerization) or adding a mixture of monomer and initiator to the catalyst. It can be seen from Table 2, runs 7 and 8, that the yields improve dramatically by employing the latter technique. In these cases, there is apparently less molecular weight control but the polydispersity index is still well below 2.

The methylation of the chain end of PMMA prepared by GTP is shown schematically in Scheme 2. It is clear that the methylation neither creates a new chiral center nor affects the stereochemistry of the asymmetric carbons adjoining the chain ends. Furthermore, if the stereochemical composition of the last three diads is known, the proportions of mm*, rm*, mr*, and rr* chain ends may be determined by

$$f_{mm^*} = f_{mmm^*} + f_{rmm^*}$$

$$f_{mr^*} = f_{mmr^*} + f_{rmr^*}$$

$$f_{rr^*} = f_{rrr^*} + f_{mrr^*}$$

$$f_{rm^*} = f_{rrm^*} + f_{mrm^*} \quad (2)$$

The ^{13}C NMR (50 MHz) spectrum of PMMA prepared under GTP conditions at −23 °C is shown in Figure 1. The assignments of various peaks are indicated in the spectrum.[16,17]

The fractions of the syndiotactic (f_{rr}), heterotactic (f_{mr}), and isotactic triads (f_{mm}) of the main chain can be obtained directly by electronic integration or direct determination of relative peak areas at 16.5, 18.5, and 21–22 ppm, respectively. The fractions of racemic (f_r) and meso diads (f_m) from the main chain can be calculated from

$$f_r = f_{rr} + 0.5f_{mr}$$

$$f_m = f_{mm} + 0.5f_{mr} \quad (3)$$

The persistence ratio, ρ, defined as

$$\rho = 2f_m f_r / f_{mr} \quad (4)$$

should be unity for a Bernoullian process. The first-order Markoff probabilities P_{mr} and P_{rm} can be calculated from[20]

$$P_{mr} = f_{mr}/(2f_{mm} + f_{mr})$$

$$P_{rm} = f_{mr}/(2f_{rr} + f_{mr}) \quad (5)$$

For a Bernoullian process, the sum of these two probabilities, $\sum P$ ($=P_{mr} + P_{rm}$), should be equal to one.

Table 3. ^{13}C NMR Triad Tacticity and Stereochemical Parameters for the Main Chain and the Chain End of PMMA Prepared by GTP

Main Chain

expt no.	T/°C	f_{mm}[a]	f_{rr}[a]	f_{mr}[a]	f_r[b]	ρ[c]	P_{mr}[d]	P_{rm}[d]	f_r/f_{r^*}
1	−96	<0.02	0.75	0.25	0.875	0.875	1.00	0.14	0.99
2	−87	<0.02	0.74	0.26	0.870	0.87	1.00	0.15	1.00
3	−78	0.031	0.71	0.26	0.840	1.03	0.81	0.16	0.97
4	−40	0.034	0.66	0.30	0.810	1.03	0.82	0.19	0.95
5	−23	0.027	0.64	0.33	0.805	0.95	0.86	0.20	0.91
6	0	0.054	0.61	0.34	0.780	1.01	0.76	0.22	0.99
7	25	0.046	0.58	0.38	0.770	0.93	0.80	0.25	0.93
8	45	0.054	0.56	0.39	0.755	0.95	0.78	0.26	1.04

Chain End

expt no.	f_{r^*}[e]	f_{rm^*}[a]	f_{mr^*}[a]	f_{rr^*}[a]	P^*_{rm}[f]
1	0.89	0.11	0.12	0.77	0.13
2	0.87	0.13	0.14	0.74	0.16
3	0.87	0.14	0.15	0.72	0.17
4	0.86	0.14	0.15	0.72	0.17
5	0.89	0.11	0.19	0.70	0.22
6	0.79	0.21	0.20	0.59	0.25
7	0.83	0.17	0.21	0.62	0.25
8	0.72	0.28	0.18	0.54	0.25

[a] Obtained directly from ^{13}C NMR. [b] Calculated from eq 3. [c] Calculated from eq 4. [d] Calculated from eq 5. [e] Calculated from chain-end triads as $f_{rr^*} + f_{mr^*}$ and eq 2. [f] Calculated from eq 6; $P^*_{mr} = 1$ since $f_{rm^*} = f_{m^*}$; no detectable mm* signal.

The main-chain tacticity data obtained along with the persistence ratio and the first Markoff parameters (Table 3) are in good agreement with previous results.[1a,5] Thus, syndiotactic content varies from ~75% at −96 °C to 56% at +45 °C. Persistence ratios are close to one.

Figure 2 is an expanded region of Figure 1 showing the methyl end group region. The two diastereotopic methyl end groups are seen, as expected, to absorb at markedly different fields (23–24 *vs* 29–30 ppm).[16] The downfield absorption is more intense, but the upfield signals are somewhat better resolved. The chain-end triad tacticity assignments (given in the spectrum) are based on well-defined oligomers of MMA.[16] The fraction of the chain-end heterotactic triads (f_{mr^*} and f_{rm^*}) are obtained directly from the NMR spectra as are the fractions of chain-end tetrads (f_{rrr^*} and f_{mrr^*}). The fraction f_{rr^*} was calculated from eq 2. The relative peak areas were determined directly by the method of cutting and weighing of the peaks after extrapolation of overlapping peaks to Lorentzian peak shapes. Both the ^{13}C NMR signals (a and b) of the methyl end groups were used for direct determination of relative peak areas.

The first-order Markoff conditional probabilities P^*_{mr} and P^*_{rm} from the chain end can be calculated from eq 6.[14]

$$P^*_{mr} = f_{rm^*}/f_{m^*}$$

$$P^*_{rm} = f_{mr^*}/f_{r^*} \quad (6)$$

For a Bernoullian process, it can be shown that generally[14]

$$f_m = f_{m^*}$$

$$f_r = f_{r^*} \quad (7)$$

and

$$P_{mr} = P^*_{mr}$$

$$P_{rm} = P^*_{rm} \quad (8)$$

Thus, for a Bernoullian process, the stereochemistry of the main chain and the chain end should be the same. Noncompliance with eq 7 but compliance with eq 8 is

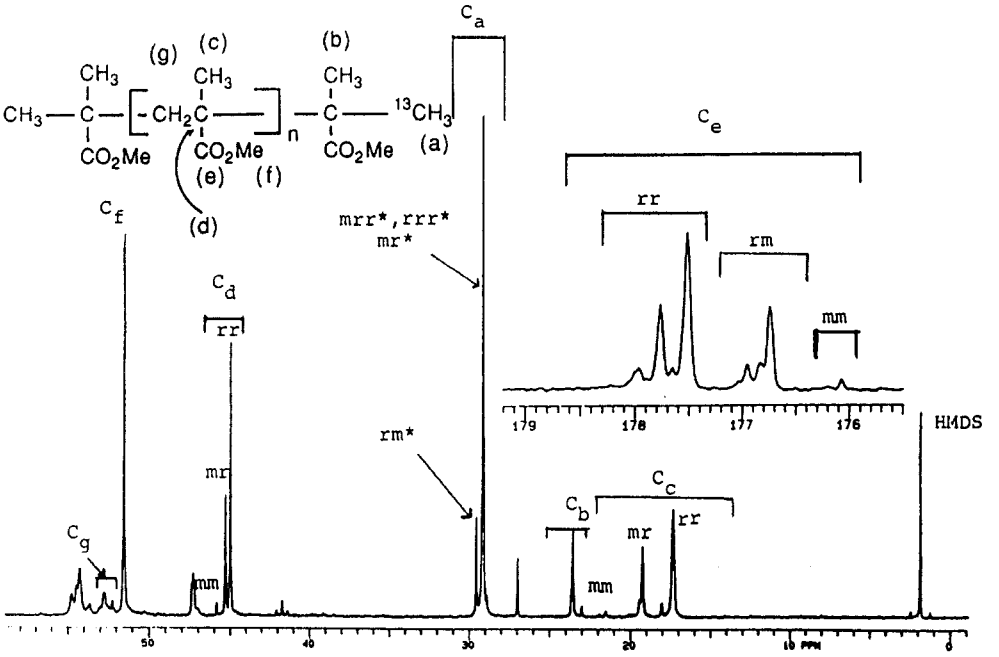
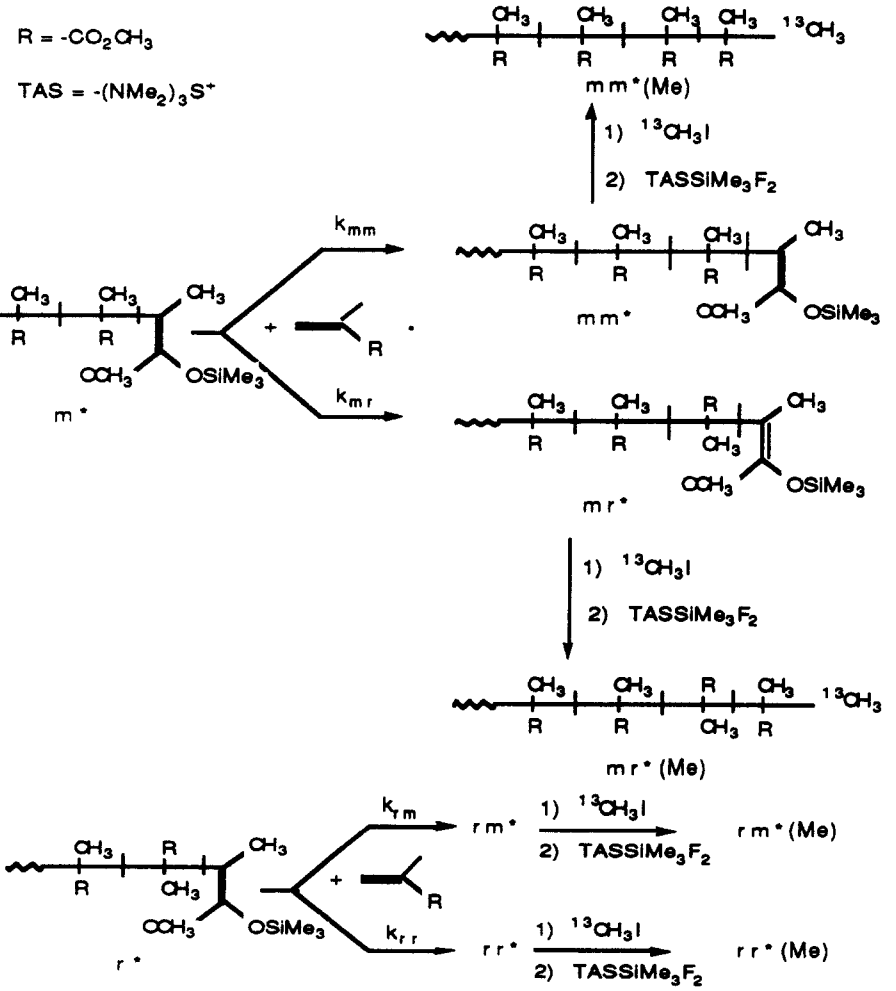


Figure 1. 50-MHz carbon-13 NMR spectrum of PMMA in $C_2D_2Cl_4$ at 90 °C prepared by GTP at −23 °C in THF.

Scheme 2. Monomer Addition and Methylation of PMMA Prepared under GTP Conditions



consistent with a first-order Markoff process. All of the tacticity results and the stereochemical parameters from the main chain and the chain end are listed in Table 3. It can be seen from this table that the persistence ratio ρ and $\sum P$ ($=P_{mr} + P_{rm}$) are close to one, consistent with Bernoullian statistics.

The fraction of racemic diads in the main chain (f_r) agrees very well with that of the chain end (f_r*) at all temperatures, indicating consistency with Bernoullian propagation statistics. In addition, the conditional first-order Markoff probability (P^*_{rm}) calculated from the chain-end stereochemistry is in excellent agreement with that from the main chain (P_{rm}), confirming consistency with Bernoullian statistics. P^*_{mr} could not be determined accurately since there was no detectable end mm* triad signal (eq 6) but should be close to one.

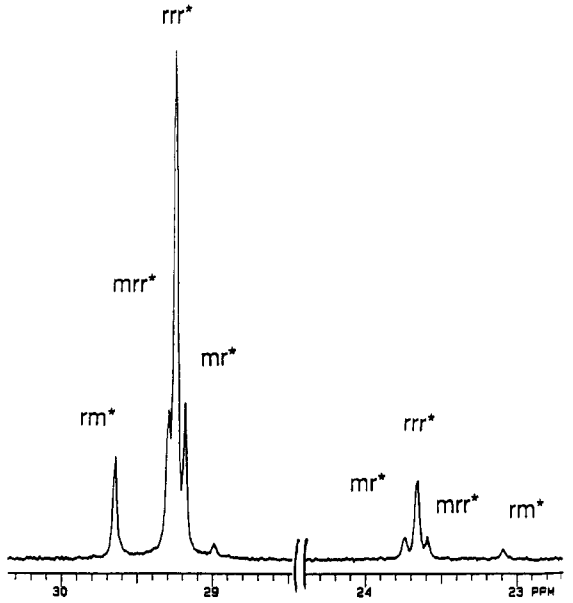
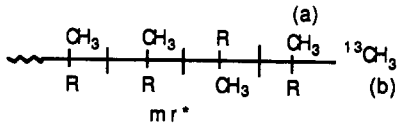


Figure 2. 50-MHz carbon-13 NMR spectrum of the ^{13}C-labeled methyl end group.

Scheme 3. The Two Diastereotopic Methyl Groups at the Chain End of PMMA: (a) Meso-like; (b) Racemic-like



R = $-CO_2CH_3$ (a) = pro-meso; (b) = pro-racemic

The temperature of methylation was either −78 or 0 °C. This temperature had no effect on the chain-end tacticity but it had a slight effect on the stereochemistry of methylation. The latter is given by the ratio of the peak areas at 29–30 ppm to that at 23–24 ppm, corresponding to the two diastereotopic methyl groups at the pro-meso and pro-racemic portions, respectively (Scheme 3).[16,17] Comparison with the analogous model oligomers of 2-isopropenylpyridine is also consistent with this.[21]

The ratio of the absorptions at 29–30 and 23–24 ppm at −78 °C is 5.70 while at 0 °C, it is 3.33. The increase in methylation stereoselectivity with decreasing temperature is not unexpected. Since methylation occurs predominantly in the pro-racemic position, the stereochemistries of methylation and polymerization are similar. Both occur predominantly in syndiotactic-like manner.

Side Reactions of Initiator and Catalyst. To probe the nature of the side reaction involving the initiator and catalyst, especially at high catalyst concentrations, an experiment was undertaken to study side products formed by reasons of the initiator and $TASHF_2$ catalyst. The initiator and $TASHF_2$ catalyst in an 11:1 molar ratio, respectively, were mixed together *in vacuo* at −78 °C in CD_3CN (the catalyst is insoluble in THF). The mixture was poured into an NMR tube after filtration *in vacuo* through a coarse glass frit and sealed. The course of the reaction was followed by ^1H NMR at room temperature (~25 °C).

Figure 3 shows the ^1H NMR spectrum (60 MHz) of the initiator (1) alone and the spectra of the reaction mixture after *ca.* 45, 75, and 120 min at room temperature. The initiator disappears with time as can be seen by the diminishing intensity of the two singlets at 1.6 ppm and the methoxy signal at 3.45 ppm. Additional peaks are seen to be appearing in the 0–0.3, 1–1.5, 2.5, and 3.6–3.7

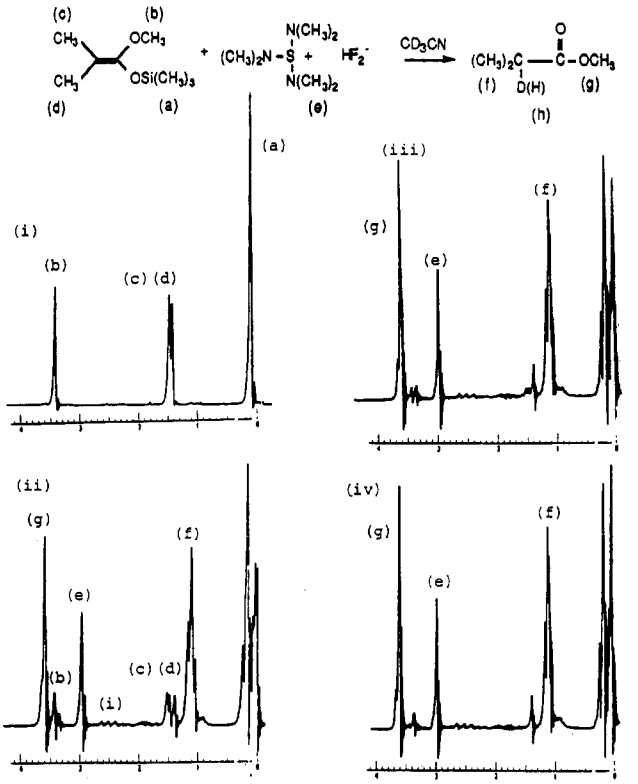
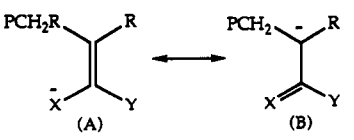


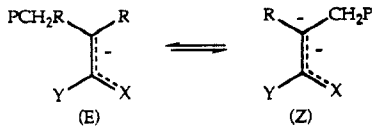
Figure 3. 60-MHz proton NMR spectra of initiator 1 and $TASHF_2$ catalyst–initiator mixture (11:1 mole ratio) in CD_3CN at 30 °C after various time intervals: (i) initiator; (ii) reaction mixture after 45 min; (iii) reaction mixture after 75 min; (iv) reaction mixture after 120 min.

ppm regions. The $TASHF_2$ catalyst had only one absorption at ~3 ppm, corresponding to the NCH_3 protons of the TAS moiety. Comparison of the ^1H and ^{13}C NMR spectra of the final products with the proton and ^{13}C NMR spectra of authentic methyl isobutyrate indicates one of the reaction products to be an 85:15 mixture of deuterated ($CD(CH_3)_2CO_2Me$) and nondeuterated methyl isobutyrate. The NMR spectra also suggest the formation of $SiMe_3F$ (doublet at 0.20 ppm downfield from TMS). The presence of methyl isobutyrate, also confirmed by a GC examination of the product mixtures, indicates deuteration of the TAS enolate by CD_3CN and protonation perhaps by the TAS cation. The side reactions effectively decrease the concentration of the initiator and thereby affect the molecular weight of the resulting polymer. The protonation of the PMMA silylketene acetal chain end by TAS cation may also occur during polymerization in THF at higher temperature along with the well-known intramolecular Claisen condensation involving the penultimate ester.

General Discussion. The anionic polymerization of vinyl monomer of the type $CH_2{=}C(R)C(Y){=}X$ (R = H or alkyl: Y, X = O, N, or C) involves anion intermediates represented by the mesomeric structures A and B:



The participation of A is substantial enough to slow down the rate of interconversion between the corresponding *E* and *Z* isomers so that the interconversion between the geometric isomers at least at low temperature (~−70 °C) is generally slow on the NMR time scale and perhaps the reaction time scale for model ester enolates and[7,21] 2-pyridine anions.[8,11] In the case of the 2-ethylpyridine



anion, representing a model for the chain end in the anionic polymerization of 2-vinylpyridine, *E–Z* interconversion is slow on the NMR time scale at temperatures as high as 120 °C. It is therefore plausible that at low temperatures (<–70 °C) and for rapid polymerization rates *E–Z* interconversion is slow on the reaction time scale also.

The relative importance of mesomeric structure A in the case of anion enolates should be even greater than for 2-pyridyl-substituted anions where structure A interferes with the aromaticity of the pyridine ring. Hence it is possible that, at least at low temperatures and for rapid polymerization rates, *E–Z* interconversion is slow on the reaction time scale for the anionic polymerization of MMA also. However, this cannot be tested readily since the PMMA anion undergoes side reactions above –70 °C. Furthermore, under our GTP conditions *E–Z* interconversion may compete with polymerization through the formation of a small amount of a carbon-silylated intermediate regardless of the occurrence of a dissociative or associative mechanism (see below). For the case where *E–Z* interconversion is slow on the NMR time scale, the monomer conformation in the transition state is the determining factor in the distribution of *E* and *Z* isomers (Scheme 4). Under these conditions, the stereochemistry of polymerization is based upon the stereochemistry of *E* and *Z* sites reacting with *s-cis* (*c*) or *s-trans* (*t*) monomers to form meso or racemic diads (Scheme 5). Since there are two enolate isomers (*E* and *Z*) that may react with *s-cis* or *s-trans* monomer to produce meso or racemic diads, there are eight possible rate constants of monomer addition. The resulting stereochemical statistics have been derived using the following additional set of assumptions:

(a) Only one type of propagating chain end is present.

(b) The *E* or *Z* sites propagate according to Bernoullian statistics and the reactivity is not dependent on the type of adjoining diad. Thus meso-*E* and racemic-*E* sites behave identically.

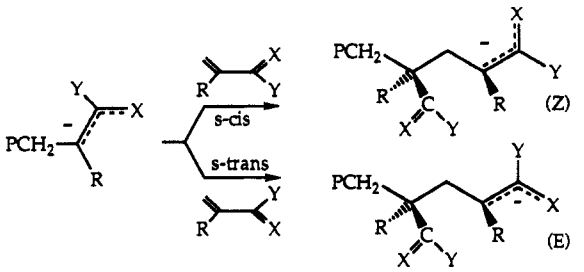
(c) Steady-state kinetics will hold for any particular species (m*Z*, mr*E*, etc.).

(d) *E* and *Z* sites react with different stereochemistries.[22-24]

Following the above model, it may be shown that the statistics are complex and generally non-Markoffian (Table 4). However, the model may conform to Bernoullian or first-order Markoff statistics under certain conditions (Table 4). The distinction with second-order Markoff statistics may be difficult to detect, particularly since both statistics may be characterized by four conditional probabilities. This makes it possible to fit most statistics rather well. However, it should be pointed out that the *E/Z* process is more realistic than "Markoff processes" since such hypothetical processes involving direct interaction of the chain end with the antepenultimate asymmetric center are not based on experimental evidence.

It appears from our method of comparison of main-chain and chain-end stereochemistry that our polymerizations produce PMMA formed according to Bernoullian statistics. Following the *E–Z* model, the results appear to conform to several limiting cases (Table 4). First the stereochemistry of monomer additions of the *E* and *Z* sites may be identical (limiting condition 1). Another possibility is that the rate of *s-trans* monomer addition to the *E* isomer is identical to the rate of *s-cis* addition to the *Z* isomer or

Scheme 4



Scheme 5. Stereochemical Pathways of Vinyl Polymerizations Involving the Addition of *s-cis* (*c*) or *s-trans* (*t*) Monomer Addition To Produce *Z* and *E* Intermediates

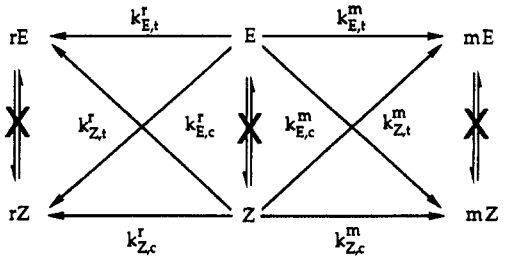


Table 4. Limiting Conditions Reducing the *E–Z* Scheme to Bernoullian or First-Order Markoff Chains

no.	condition (Scheme 4)	statistics
1	$k^m_{E,t} = k^m_{Z,t}$, $k^m_{E,c} = k^m_{Z,c}$, $k^r_{E,t} = k^r_{Z,t}$, $k^r_{E,c} = k^r_{Z,c}$	Bernoullian[a]
2	$k^m_{E,t} = k^m_{Z,c}$, $k^m_{E,c} = k^m_{Z,t}$, $k^r_{E,t} = k^r_{Z,c}$, $k^r_{E,c} = k^r_{Z,t}$	Bernoullian[b]
3/4	$k^m_{Z,t} = k^r_{Z,t} = 0$ or $k^m_{E,c} = k^{rE,c} = 0$	Bernoullian[c]
5	$k^m_{Z,t} = k^m_{Z,c} = k^r_{E,t} = k^r_{E,c} = 0$	1st Markoff[d]
6	$k^m_{E,}{}^t = k^m_{E,c} = k^r_{Z,t} = k^r_{Z,c} = 0$	1st Markoff[e]

[a] *E* and *Z* sites show identical behavior. [b] *s-trans* addition to *E* is identical to *s-cis* addition to *Z* and vice versa. [c] Only *Z* or *E* sites are present, respectively. [d] *E* sites lead to m diads, and *Z* sites lead to r diads. [e] *E* sites lead to r diads, and *Z* sites lead to m diads.

vice versa (limiting condition 2). This accidental equality of rates is possible but not very likely. The third limiting condition reducing the *E–Z* scheme to Bernoullian statistics, namely, the presence of only *Z* or *E* sites, appears unlikely in this case since a 70/30 *E/Z* mixture of silylketene acetals is found in the GTP of MMA.[10] Finally, it is possible that the rate of *E–Z* interconversion is competitive with polymerization. Under such conditions, Bernoullian statistics should result also. It is not trivial to decide which of these mechanisms prevails in the present case. Case 1 seems most straightforward, but this interpretation would seem to be inconsistent with a substantial body of data showing that *E* and *Z* isomers often react with different stereochemistries.[22-24] Case 1 should not be ruled out, however, until more information is available on the kinetics and stereochemistry of the individual *E* and *Z* sites. For instance, the large TAS counterion would preclude any intramolecular cation coordination by the penultimate Lewis base sites (such as C=O) on the chain. Furthermore, the TAS ion may shield the chain end from other interactions as well so that *E* and *Z* anions react in an identical manner. In fact, results reported by Brittain appear to indicate that for GTP of MMA in the presence of tetrabutylammonium bibenzoate the *E* and *Z* isomers react with identical rates. This suggests but does not prove that the stereochemistry of monomer addition of *E* and *Z* sites is identical as well. In this regard, it is of interest that the MMA anionic polymerization in THF at –78 °C in the presence of K^+ or Cs^+ ion is non-Bernoullian, whereas in the presence of K^+ complexed with (2.2.2)cryptand the

polymerization is once again Bernoullian.[7] The stereochemistry of MMA polymerization in the presence of K^+-(2.2.2) and TAS^+ should indeed be similar since both ions are essentially bulky organic cations. The triad tacticities in this case (mm = 0.02, mr = 0.31, rr = 0.67) are indeed in agreement with those observed for the above TAS enolate system (mm = 0.03, mr = 0.26, rr = 0.71) (Table 3). This would appear to be consistent with a recently proposed dissociative mechanism for group-transfer polymerization.[25] Finally, rapid *E–Z* interconversion could account for the data. Studies aimed at this problem are being planned.

In conclusion, it has been shown that the stereochemistry of the polymerization of MMA carried out under GTP conditions is consistent with simple Bernoullian statistics. In addition, it has been shown that a comparison of the stereochemistry of the main chain with that of the chain end of a polymer is a sensitive and independent method for the verification of the statistics of vinyl polymerization and is applicable to systems other than anionic polymerization.

Acknowledgment. Support for this work was provided by the NSF DMR Polymers Program.

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